Indonesian Journal of Chemistry and Environment
Vol. 6, No. 2, December 2023, pp. 83~94
e-ISSN: 2599-3186

Synthesis of Natural Zeolite/ZnO and Its Photodegradation Activity on Congo Red

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Article Info

Article history:

Received Oct 12th, 2023
Revised Dec 6th, 2023
Accepted Dec 12th, 2023

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ABSTRACT

Dyes are the most common compound used in the textile industry. Dyes consisted of azo compound that is difficult to be degraded. Undegradated azo compound, such as congo red, danger for the environment. An alternative effort to handle congo red waste must be conducted. Natural zeolite/ZnO is a material that can be used to degrade congo red to be simpler compound. Based on the analysis, the characters of natural zeolite/ZnO are hexagonal wurtzite structure, particle size 24.264 nm, band gap energy 2.96 eV. The highest degradation percentage in photodegradation activity of natural zeolite/ZnO on congo red is 99.41%.

Keyword: Natural zeolite/ZnO, degradation percentage of Congo Red

1. INTRODUCTION

Dyes in textile industrial consist azo compounds that are difficult to be degraded due to the stabilsynthetic aromatic compounds. One of the dyes in textile industry is congo red. Congo red is sodium salt of benzidineadiazo-bis- naphthylamine-4 sulfonic acid (Figure 1) with the molar mass 696.66 gram/mol (Sawhney & Kumar, 2011. Congo redi is water soluble and ethanol, slightly soluble in aceton and insoluble in ether and xylene (Yaneva & Georgieva, 2012).

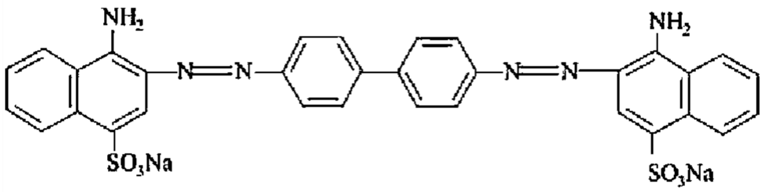

Figure 1. The strucyure of congo red

Congo red is high toxic, mutagenic and carsinogenic compound that may cause anaphylactic shock and cancer. Based on that fact, congo red waste, especially that come from textile waste, must be handled carefully before being released to the environment.

Many procedurs have been proposed to reduce industrial textile waste, such as coagulation, precipitation and adsorbtion. These methods are simple and cheap in cost but still have several shortages. Alternative methods are needed to overcome those shortages. One of the alternative methods to reprocess the textile industry is photodegradation.

Photodegradation is a process to decompose a compound to be simpler compound with the presence of catalyst and photon energy. In photodegradation methode, dye waste is decomposed to be simpler compound using semiconductor photocatalyst and sun radiation. If the photon ray hit the semiconductor catalyst, electrons from valence band move to conduction band and leave holes in valence band. Electron in conduction band will produce superoxide ion and hydroxyl radical that used in photodegradation (Titdoy et.al., 2015). The dedragation of congo red, based on GC-MS analysis is shown in Figure 2 (Gomathy et.al., 2009)

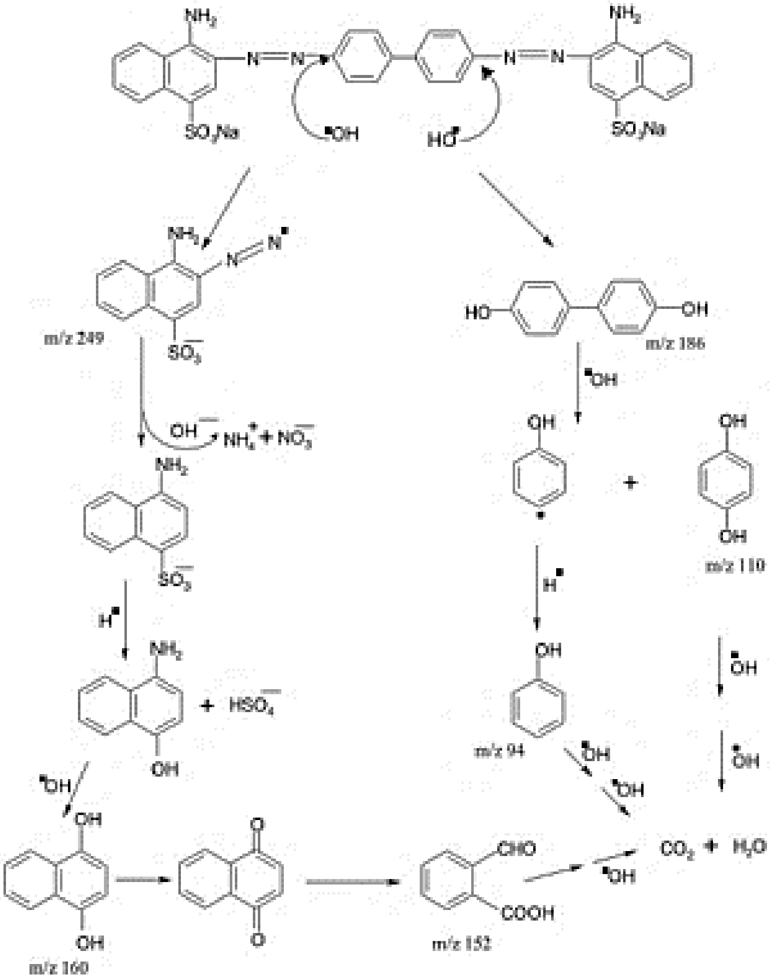

Figure 2. the mechanism of the degradation of congo red (Gomathy et.al., 2009)

Activity of photodegradation may be increased by using semiconductor material, such as zinc oxide (ZnO). Zinc oxide is white crystal with band gap energy 3.3 – 3.7 eV. Zinc oxide is usually used in the electronic field, catalyst, biotechnology and so on. Zinc oxide is an n-type semiconductor with high transmittance, high chemical and mechanical stability. The form of ZnO nanoparticle may cubic, rocksalt cubic and hexagonal, which the hexagonal is the most stbale (Fazmar, 2009). The lattice parameters of zinc oxide wurtzite are: a = b = 0.3249 nm and c = 0.52042 nm with the ratio of c/a = 1.602, the angle α = 109.46° and the density = 5.675 g/cm^3 (cm^3 (Tüzemen & Gür, 2006). The structure of ZnO wurtzite is shown in Figure 3.

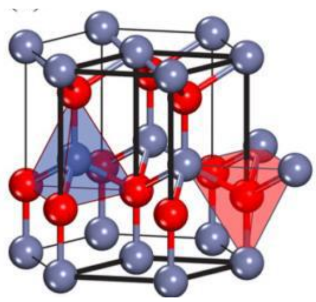

Figure 3. Structure of ZnO wurtzite

The photocatalysist activity of zinc oxide may be increased by dopping it to the support, such as zeolite. Zeolite is a tetrahedral alumina silicate mineral. Based on the structure, zeolite may be used as an adsorbent, thermal catalyst, ion exchange and catalyst support (Sutarti and Rahmawati, 1994). When metal oxide, such as TiO_2, ZnO, CuO and CaO, are dropped onto the zeolite surface, may degrade the organic compound. Based on the fact, zeolite is extensively used to process liquid waste. Before using, natural zeolite must be activated by strong acid or base solution. Mordenite ($Na_8Al_8Si_{40}O_{96}.24H_2O$) type of natural zeolite is shown in Figure 4 (Farias *et al.*, 2015).

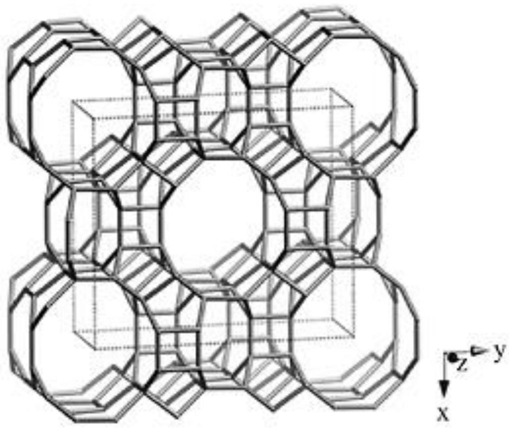

Figure 4. Structure of modernite

2. RESEARCH METHOD

Zinc oxide was prepared by immersing 18 g of $Zn(CH_3COO)_2.2H_2O$ into 32 mL of ethanol. Tthe mixture was then stirred and heated in a flask for 2 hours at 76 ^oC. A 90 mL NaOH 2M was slowly added into the mixture and stirred fo 1 hour. After 1 hour, the mixture was decanted with filter paper to get ZnO. The precipitation was dried in an oven for 1 hour at 110^oC, and then calcined in muffle furnace at 450 ^oC for an hour. The synthesized ZnO was then characterized by using XRD and FTIR.

The grinded zeolite wa sieved by 150 mesh siever, and then immersed into aquadest with the ratio of zeoliteto aquadest was 1:3. The mixture was then stirred and heated at 90 ^oC for 2 hours. The yielded precipitation was dried in an oven at 120 ^OC for 5 hours, and then calcined in muffle furnace at 300 ^oC for 2 hours. The precipitation was immersed into 1 M NaCl solution with the ratio of precipitation to NaCl solution is 1:4 and heated at 80 ^oC for 2 hours. The precipitation was decanted and dried in an oven at 120 ^oC for 5 hours, and then calcined for 3 hours at 300 ^oC. The physical and chemical activated zeolite was characterized by using XRD and FTIR.

Natural zeolite/ZnO was prepared by mixing activated zeolite with kristal $Zn(CH_3COO)_2.2H_2O$ powder and ethanol with the ratio 4:2:15 respectively. The mixture was stirred and heated at 50 ^oC for 2 hours. A60 mL of 0.1 M NaOH solution was added to the mixture and stirred for an hour. The resulting precipitation was separated, dried at 120 ^oC for 5 hours and then calcined at 400 ^{o} C for 2 hours. Nature zeolite/ZnO material was characterized by using XRD, FTIR, UV-Vis and SEM-EDX.

Protodegradation of congo red by natural zeolite/ZnO was conducted under UV irradiation. A 0.1 gram natural zeolite/ZnO was immersed into 10 mL of 10 ppm congo red solution. The UV irradiation was taken at -30 (dark condition), 0, 30, 60, 90 and 120 minutes. After UV irradiation, themixture was centrifused and analyzed by UV-Vis spectrometer at maximum wave length to obtain the absorbance of congo red after the degradation.

3. RESULTS AND ANALYSIS

The natural zeolite/ZnO material (Figure. 5) is successfully prepared by precipitation methode use activated natural zeolite and $Zn(CH_3COO)_2.2H_2O$ as the precursors.

Figure 5. Material natural zeolit/ZnO

3.1. The characterization of natural solite/ZnO material

a. X-Ray Diffraction

Crystalinity of synthesized ZnO is investigated by usingXRD Miniflex 600, range 4^o – 80^o, radiation CuKα, voltage 40 kW and current 15 mA. A diffractogram of synthesized ZnO is shown in Figure 6, whereas diffraction pattern, based on Origin software, is shown in Figure 6.

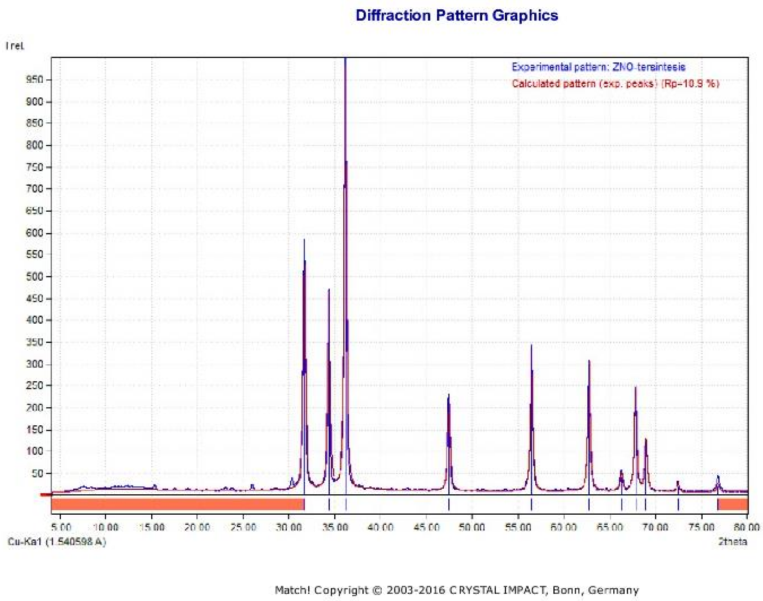

Figure 6. Difractogram of synthesized ZnO

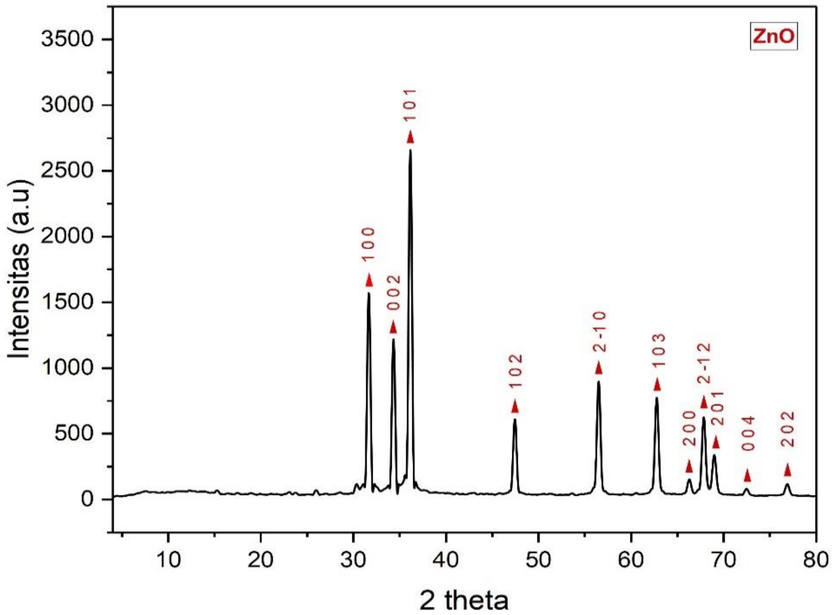

Figure 71. Diffraction pattern of synthesized ZnO

Diffraction pattern on ZnO shows the value of 2θ = 31,69°; 34,36°; 36,17°; 47,49°; 56,50°; 62,77°; 66,32°; 67,84°; 68,98°; 72,48° dan 76,84°. The 2θ value of the synthesized ZnO is matching with COD (*Crystallography Open Database*) data No. 00-101-1258 and indicates that the peaks are characteristic of ZnO hexagonal wurtzite. The high peaks indicates that ZnO is crystallin. Diffraction peaks in accordance with crystall field (100), (002), (101), (102), (103), (200) and (201), follows standard pattern ZnO of *Joint Committee on Powder Diffraction Standart* (JCPDS) No. 036-1451. Lattice parameters are investigated by Rietica software and the result shows that in synthesized ZnO match with the data of *American Mineralogist Crystal Structure Database* (AMCSD) No. 1011258.

The diffraction peaks of refinement by Rietica software is shown in Figure 8.

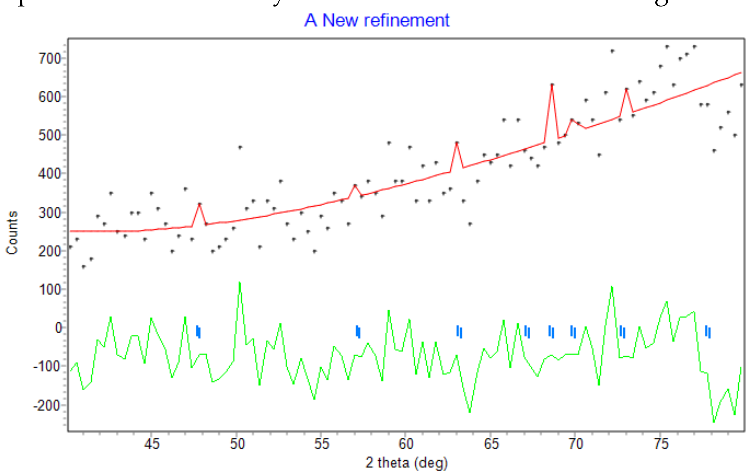

Figure 82. The refinement result of synthesized ZnO

The result of refinement process is fit with pattern with the diffraction pattern data of *American Mineralogist Crystal Structure Database* (AMCSD) No. 1011258., with a = b = 0,360 Å dan c = 0,193 Å. It indicates that diffraction pattern of the synthesized ZnO is hexagonal. Based on Scherres equation, crystal size of ZnO is 26.063 nm and can be classified as nano particle.

The diffraction pattern of unactivated and activated natural zeolite are shon in Figure 9 and Figure 10.

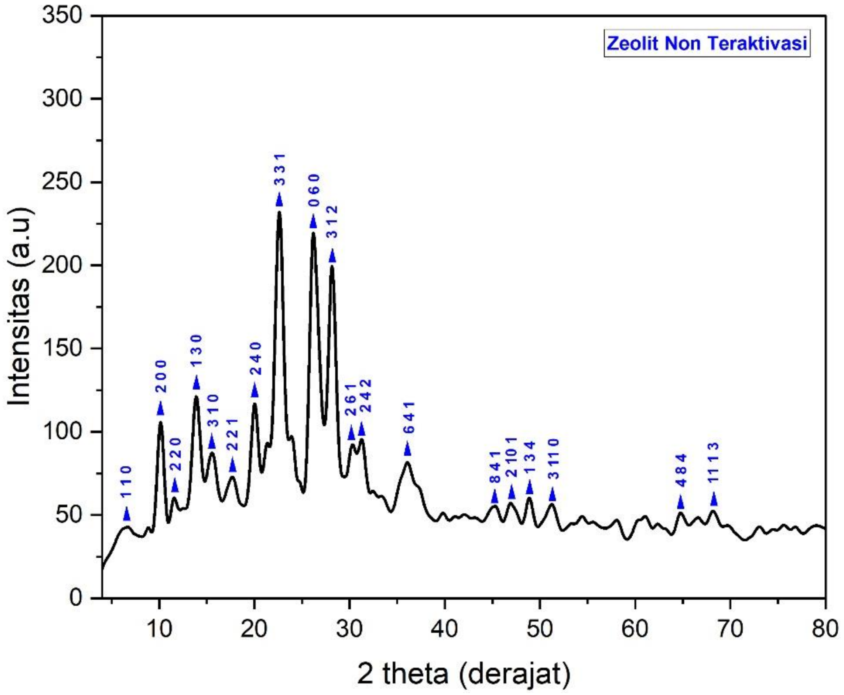

Figure 9. Diffraction pattern of unactivated natural zeolite

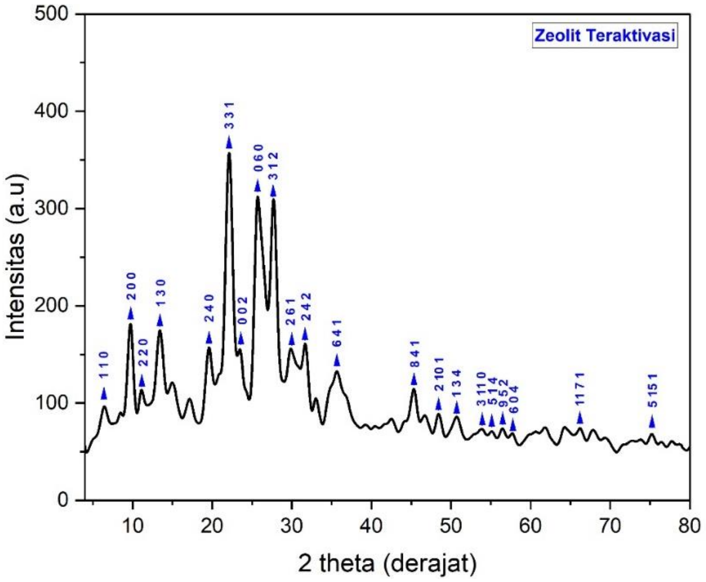

Figure 10. Diffraction pattern of activated natural zeolite

Based on the diffraction pattern in Figure 9 and Figure 10, it can be concluded that the two diffraction patterns are similar. It indicates that physical and chemical activation did not damage the structure of the natural zeolite. The 2θ values of activated natural zeolite fit with COD (Crystallography Open Database) No. 00-900-3355, that means the natural zeolite is ortorombic mordenite and the formula is $Al_{1.5}H_{30}Na_{1.37}O_{28.86}Si_{10.5}$.

Diffraction pattern of natural zeolite/ZnO is shown in Figure 11.

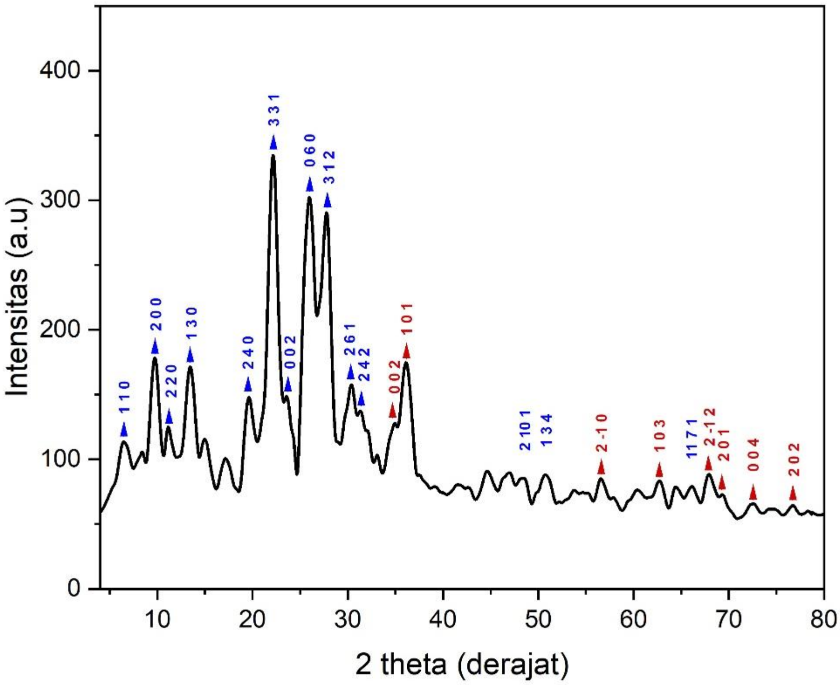

Figure 11. Diffraction pattern of natural zeolite/ZnO material

The 2θ values of natural zeolite/ZnO match with the data of COD (Crystallography Open Database) No. 00-900-3355 (modernite zeolite) and No. 00-101-1258 (ZnO), with the percentage of modernite and ZnO are 68.75 % and 31.43 % respectively. Based on Scherrer equation, the crystal size of unactivated natural zeolite, activatd zeolite and natural zeolite/ZnO are 20.645 nm, 16.959 nm and 24.264 nm respectively. It can be concluded that the crystals are nanoparticles in category.

b. FTIR

The FTIR spectra of natural zeolite/ZnO is shown in Figure 12, whereas the interpretation in Table 1.

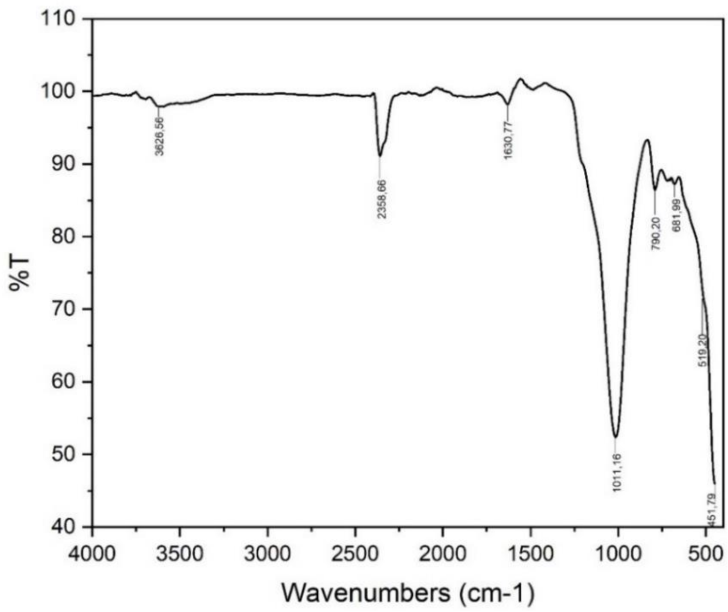

Figure 12. FTIR spectra of natural zeolite/ZnO

Table 1. Intepretation of FTIR spectra of natural zeolite/ZnO

Wave number (cm^{-1})	Intepretation
3626.56	O-H stretching
2358.66	Si-OH vibration
1634.35	Zn-O-Zn stretching
1011.16	Si-O-Si or Zn-O-Si stretching
789.56 and 668.37	O-Si-O or O-Al-O symmetry vibration
519.20 and 451.79	Zn-O stretching

Based on Table 1, it`s showed that ZnO is successfully dopped onto natural zeolite surface.

c. UV-Vis Spectroscopy

Absorbance spectrum of naturalzeolite/ZnO is shon in Figure 13.

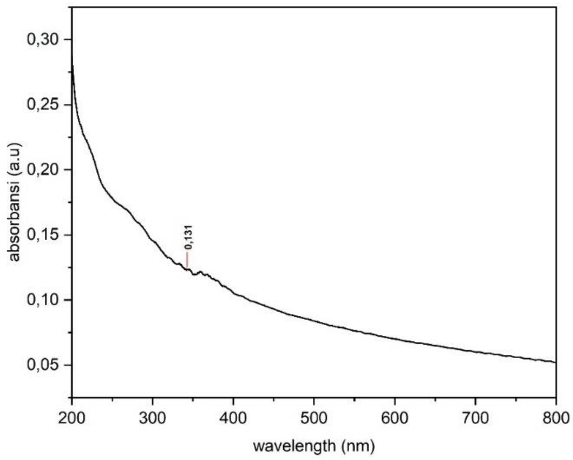

Figure 13. Absorbance spectrum of natural zeolite/ZnO

Natural zeolite/ZnO absorp energy in UV area, with maximum wavelength and absorbance are 343 nm and 0.131 respectively. Band gap energy of natural zeolite/ZnO is determined based on the absorbancy data by using Tauc Plot methode (Figure 14)

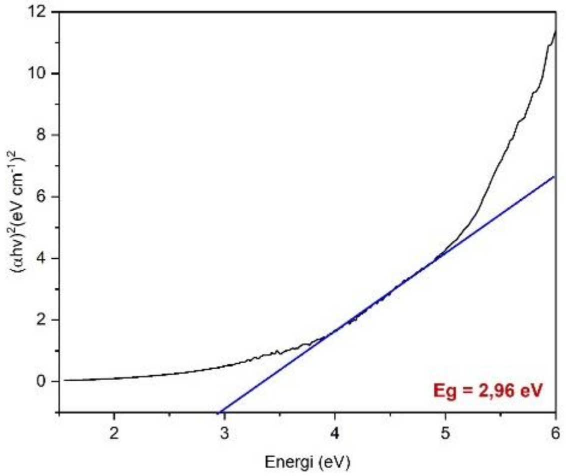

Figure 14. Graph of determining of band gap energy of natural zeolite/ZnO

Based on Figure 14, the band gap energy of natural zeolite/ZnO is 2.96 eV and indicates that the dopping of ZnO onto zeolite surface decrease the band gap energy of ZnO (3.3 – 3.7 eV). Zeolite disperses ZnO onto the surface and increase the surface area of photocatalyst, so the band gap energy is decrease.

d. SEM-EDX

The magnification of 1000, 3000, 5000 and 10000, depth of field 4 – 0.4 mm and resolution1-10 nm are conducted in SEM analysis of natural zeolite/ZnO (Figure 15)

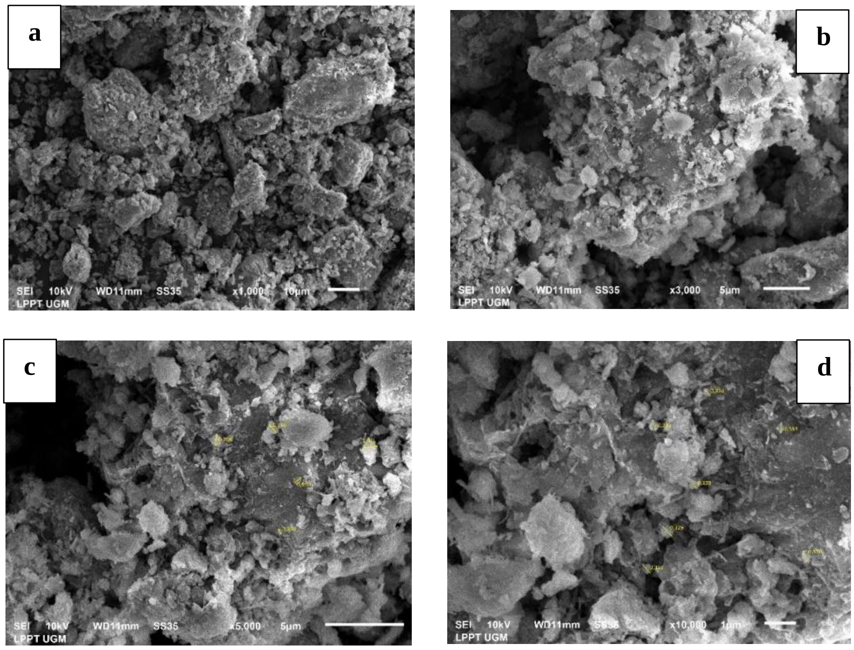

Figure 15. SEM analysis of naturalzeolit/ZnO with the magnification a)1000, b) 3000, c) 5000 and d) 10,000

Morphology analysis shows that there are agglomerates (0.384 -1.076 μm in size) and small particles (0.313 – 0.370 μm in size) dispersed randomly around it. The agglomerate is supposed to be zeolite, and the small particle ZnO. The EDX spectrum of natural zeolite/ZnO is shown in Figure 16, whereas mass percentage in Table 2.

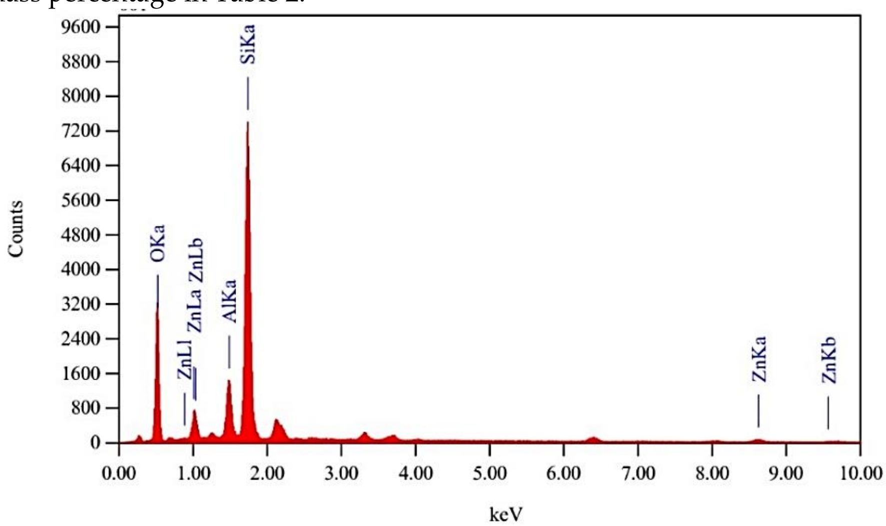

Figure 15. EDX spectrum of natural zeolite/ZnO

Table 2. Mass percentage and dispersion energy of natural zeolite/ZnO

Element	Percentage	Dispersion Energy
O	45,03%	0,525 keV
Si	39,18%	1,739 keV
Al	6,62%	8,630 keV
Zn	9,18%	1,486 keV

Based on Figure 15 and Table 2, it can be concluded that ZnO is successfully dopped onto the zeolite surface.

3.2. Activity test of natural solite/ZnO material on the photodegradation of congo red

Maximum wavelength of congo red is shown in Figure 16.

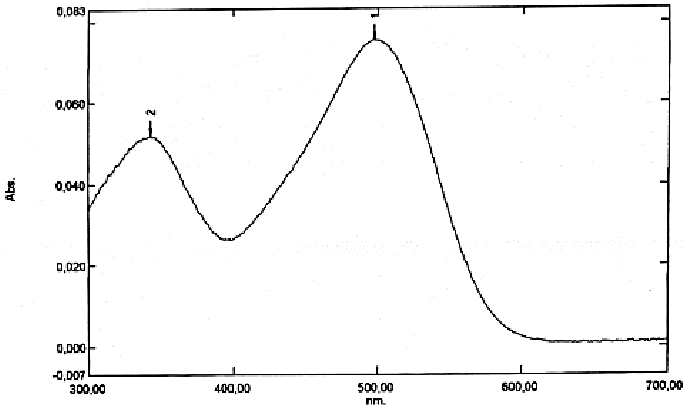

Figure 16. Maximum wave length of *Congo Red*

Based on Figure 16., maximum wave length of congo red is 497.5 nm and the absobance is 0.076.

The absorbance of standard congo red solution is shown in Table 3 and the standard curve of congo redis shown in Figure 17.

Table 3. The absorbance of standard congo red solution

Concentration (ppm)	Absorbance
0	0,000
1	0,038
2	0,076
3	0,109
4	0,156
5	0,187

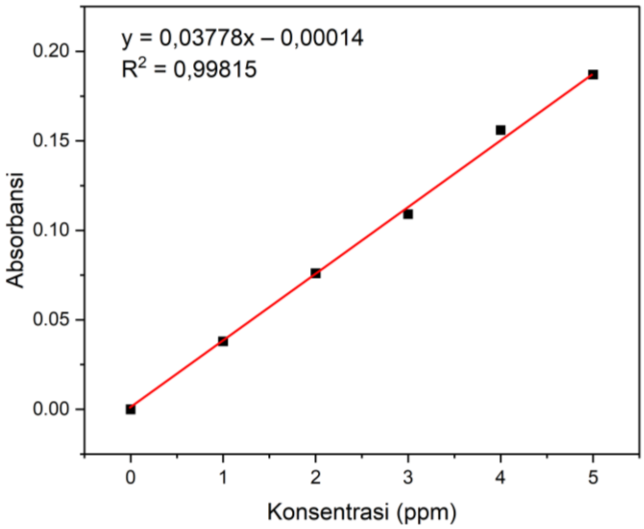

Figure 17. Standard curve of congo red

The linear regression of standard curve of congo red is y = 0,03778x – 0,00014, with correlation coefficient (R^2) is 0,99815. It means, the standard curve of congo red fulfil the SNI 06-6983.31-25 with the correlation coefficient ≥ 0,97.

The result of congo red degradation by using natural zeolite/ZnO is shown in Table 4.

Table 4. The degradation of congo red under UV irradiation

No.	Irradiation time (minute)	Initial absorbance	Initial concentration (ppm)	Final absorbance	Final concentration (ppm)	Degradation percentage (%)
1.	- 30	0.362	9.5855	0.198	5.2446	45.29
2.	0	0.362	9.5855	0.362	9.5855	0.00
3.	30	0.362	9.5855	0.131	3.4711	63.79
4.	60	0.362	9.5855	0.051	1.3536	85.88
5.	90	0.362	9.5855	0.023	0.6125	93.61
6.	120	0.362	9.5855	0.002	0.0566	99.41

In dark conditions (-30 minute), the degradation is 45.29 %, due to the adsorption on the catalyst surface. The absence of photons makes no hydroxyl radical formed. Under UV irradiation, the greater the irradiation time, the greater the hydroxyl radical formed. Hydroxyl radical is a strong oxidazing agent that contributes to the degradation process. The greater the hydroxyl, the greater the congo red degradated. The highest percentage of photodegradation of ongo red is obtained at 120^{th} minute, with the degradation percentage 99.41%. based on the photodegradation values, it can be concluded that material of natural zeolite/ZnO has a good catalytic activity on the photodegradation of congo red under UV irradiation.

4. CONCLUSION

The synthesized natural zeolite/ZnO by precipitation methode has the following characteristics: structure hexagonal wurtzite, particle size 24.264 nm, band gap energy 2.96 eV. The highest degradation percentage in photodegradation activity of natural zeolite/ZnO on congo red is 99.41%.

ACKNOWLEDGEMENTS

A special thank you to the dean of Mathematics and Natural Sciences Faculty of State University of Yogyakarta for funding this research.

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